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Rapid Distinguishing between Rhodium and Palladium in Highly Contaminated Waters Using Amperometry

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A rapid, electrochemical method for determination of $RhCl_3$ and $PdCl_2$ was developed. With respect to behavior of studied PGEs in the environment, we chose acetate and borate buffer with different pH to investigate their electrochemical behavior using planar glassy carbon electrode. Rh was determined without difficulties in the first step, which was based on the application of borate buffer (pH 7) and detection potential of 1000 mV. In the second step mobile phase is changed from borate to acetate buffer (pH 4) and detection potential is increased to 1100 mV. Based on these, we are able to distinguish the metals.

Keywords: Flow Injection Analysis with Electrochemical Detection; Hydrodynamic Voltammograms; Rapid Distinguishing; Palladium; Rhodium

1. INTRODUCTION

Palladium and rhodium belong to the platinum group elements (PGEs) having strong catalytic properties, i.e. they may be oxidized difficultly. This fact is connected with their physico-chemical properties resulting in resistance against chemicals and stable electrochemical behavior [1]. Thanks to these unique properties, they could surely be important in the power generation, transportation, healthcare and a plenty of other areas, such as in electrochemical, automotive, chemical, petroleum, and aerospace industries in the future. In medicine, PGEs have been proved to show inertness, low

corrosivity (and thus biocompatibility and durability), and good biomechanical properties [2]. Due to these properties, platinum or platinum-containing alloys are used for medical devices, such as stents, spinal fixation, and hip or knee implants.

Based on the above mentioned facts it is clear that they are increasingly utilized for various purposes, which can cause their accumulation and thus negative impact on the environment. Car catalysts, jewellery and other branches of industry, such as petroleum, electric, gas, and chemical industries participate significantly on the contamination of the environment with PGEs [3,4]. The presence of PGEs in water has been shown by several studies [5-7]. The environmental risk of PGEs depends on their bioavailability. Whereas insoluble or poorly soluble compounds demonstrate only low risk for the environment, water-soluble compounds are taken up easily by organisms; they enter the food chain and cause serious environmental problems.

Analysis of PGEs in the environment is relatively difficult, especially due to heterogeneity and complexity of the samples and low concentrations of PGEs in the environmental samples. In order to analyze the reliably of the environmental samples, technical improvement of analytical instruments to determine PGEs is quite necessary. Spectrophotometry which is a part of atomic absorption spectrometry (AAS) is the most commonly used method for detection of PGEs. Flow injection analysis of platinum based on the color reaction of Pt(IV) with $SnCl_2$ in the HCl medium was also described [8] together with FIA-FAAS method [9,10] with the limit of detection 150 $ng.mL^{-1}$. However, these methods usually require pre-concentration step or treatment of the sample. Liquid chromatography (LC) represents another suitable method for determination of PGEs. The determination of PGEs using the LC method usually requires a pre-column derivatization with 2,4-dihydroxybenzylidenethiorhodanine (DHBTR) [11] or 4-carboxylphenyl-thiorhodanine (CPTR) [12] with the limits of detection for palladium, platinum and rhodium in the units of $ng.L^{-1}$. The reverse-phase liquid chromatography [13,14], normal-phase liquid chromatography [13], and ion exchange chromatography [15] coupled with UV detection (HPLC-UV) have been proved to determine PGEs in different types of samples. Electrochemical techniques represent a group of highly advantageous techniques to determine PGEs, especially due to high sensitivity that is based on the catalytic properties of platinum compounds [16]. Adsorptive stripping voltammetry provides the low limits of detection for PGEs and thus enables us to determine platinum in water at very low levels [17,18]. The hanging drop mercury electrode (HDME) [19,20], modified carbon paste electrode (CPE) [21] or a glassy carbon electrode (GCE) [7] are also used to determine PGEs in the samples. To provide high throughput detection of PGEs, the connection with flow injection analysis (FIA), which is a simple and feasible analytical technique with the capacity for very rapid analysis of samples with the possibility of partial or complete automation, could be convenient. The aim of this study was to optimize the FIA-ED with a glassy carbon electrode as a working electrode to characterize electrochemically platinum(II), platinum(IV), palladium(II), rhodium(III), oxaliplatin, carboplatin, and cisplatin. To achieve the best detection conditions we also tested the effect of the flow rate and buffer in their detection. The optimized method was further used for determination of the above-mentioned platinum, palladium and rhodium compounds in the samples of water. Developed method may serve as a rapid, screening, method for analysis of waters suffering from industrial contamination or ecological catastrophe.

2. EXPERIMENTAL PART

2.1. Chemicals

Standards of $PtCl_2$, $PtCl_4$, $RhCl_3$ and $PdCl_2$ were obtained from Sigma-Aldrich (St. Louis, MO, USA). Oxaliplatin was purchased from Merck&Co (Whitehouse Station, NJ, USA), carboplatin Teva was obtained from Teva UK (Castleford, United Kingdom), and cisplatin EBEWE was from EBEWE Pharma (Unterach am Attersee, Austria). Other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) in ACS purity (meets standards of the American Chemical Society) unless noted otherwise. Stock standard solutions of PGEs (1 $mg.mL^{-1}$) were prepared in ACS water with 1 % HCl (*v/v*) added to increase solubility of PGEs. The working standard solutions of analyzed PGEs were prepared daily immediately prior to use by dilution of stock solutions to final concentration of 10 $\mu g.mL^{-1}$. All the solutions were prepared in deionized water, obtained by use of reverse osmosis equipment Aqual 25 (Aqual s.r.o., Brno, Czech Republic). Deionized water was further purified by using an apparatus Direct-Q 3 UV Water Purification System equipped with a UV lamp (Millipore, Billerica, Massachusetts, USA). The resistance was set to 18 $M\Omega.cm^{-1}$. The value of pH was measured using a pH meter WTW inoLab equipped with terminal Level 3 (Weilheim, Germany), controlled by MultiLab Pilot software (Weilheim, Germany).

2.2. FIA-ED system

The instrument for flow injection analysis with electrochemical detection (FIA-ED) consisted of a solvent delivery pump operating within the range of 0.001-9.999 $mL.min^{-1}$ (Model 582 ESA Inc., Chelmsford, MA, USA) and an electrochemical detector. The electrochemical detector includes one low-volume flow-through analytical cell (Model 5040, ESA, USA), which consists of a glassy carbon electrode as a working electrode, a hydrogen-palladium electrode as a reference electrode and an auxiliary electrode, and Coulochem III as a control potentiostat module. The sample (20 μL) was injected using an autosampler (Model 542, ESA, USA). Buffers with different pH, chosen for the ability to maintain a constant conditions (pH) during the measurements (acetate buffer with pH 3.5; 4.0; 4.5, 5.5, and borate buffer with pH 7; 8 and 9 respectively) were used as mobile phases (optimized conditions see below). Detection was carried out at different potentials (100; 200; 300; 400; 500; 600; 700; 800; 900; 1000; 1100; and 1200 mV) to obtain hydrodynamic voltammograms (HDVs) of individual PGEs. Optimal potential obtained from HDVs was used to perform more detailed measurements to identify the most suitable detection potential. Flow rate of a mobile phase was optimized according the results of the FIA-ED optimization and was performed within the range from 0.6 to 1.4 $mL.min^{-1}$. 1% HCl in ACS water was used as a blank. The data obtained were analyzed with the Clarity software (Version 1.2.4, Data Apex, Czech Republic). The experiments were carried out at a temperature of 25 °C. A glassy carbon electrode was polished mechanically by alumina (0.1 μm, ESA Inc., USA) and sonicated at room temperature for 5 min using a Sonorex Digital 10 P Sonicator (Bandelin, Berlin, Germany) at 40 W each seventh day of continual measurement.

2.3. Mixed samples preparation

Samples of PGEs were prepared immediately prior to use from stock solutions (of concentration of 1 $mg.mL^{-1}$) which was prepared in water of ACS purity. Calibration curves were further used for quantification of PGEs in real sample. Mixed samples were prepared with real sample of water, obtained from river Svratka as a mixtures of Rh : Pd, Pd : Rh, Rh : Pt, Pt : Rh, Pd : Pt, and Pt : Pd in the following ratios 1 : 1; 1 : 10; 1 : 50, and 1 : 100, where number 1 represents the concentration of 10 $\mu g.mL^{-1}$ (it means 10 corresponds to 100 $\mu g.mL^{-1}$, 50 to 500 $\mu g.mL^{-1}$, and 100 to 1000 $\mu g.mL^{-1}$). Cisplatin was used as a representative of platinum compounds, because it is one of the most commonly used antineoplastic drugs used in the therapy of solid tumors. Superficial water samples were taken with a portable suction pump made of stainless steel and of which would not yield contamination with the four elements to be determined. FIA-ED analyses were carried out under conditions optimized in the previous measurements in order to obtain the optimal signals: flow rate 1.0 $mL.min^{-1}$, borate buffer of pH 7, and potential of 1000 mV for rhodium analysis and acetate buffer of pH 4, flow rate 1.0 $mL.min^{-1}$ and potential of 1100 mV for determination of palladium and platinum. The signals obtained were further evaluated. Height of signals was used to quantify the amount of PGEs in the mixed samples according to the calibration curves. Results were also evaluated statistically.

2.4. Mathematical treatment of data and estimation of detection limits

Mathematical analysis of the experimental data and their graphical interpretation were carried out by the Microsoft Office tools (MS Excel®, MS Word®, and MS PowerPoint®). All results were expressed as a mean ± standard deviation (S. D.) unless noted otherwise. The detection limits (3 signal/noise, S/N) were calculated according to Long and Winefordner [22], whereas N was expressed as a standard deviation of noise determined in the signal domain unless stated otherwise.

3. RESULTS AND DISCUSSION

3.1. Optimization of flow rate

Firstly, the effect of the flow rate on determination of PGEs was evaluated at 0.6; 0.8; 1.0; 1.2 and 1.4 $mL.min^{-1}$. Fig. 1A-G shows the effect of the flow rate which is indicated by the height of signal of oxaliplatin, carboplatin, cisplatin, $PtCl_2$, $PtCl_4$, $RhCl_3$ and $PdCl_2$, respectively. The flow rate was established to be one of the most important parameters in analysis. Higher flow rate (in our case flow rate values higher than 1.0 $mL.min^{-1}$) caused a shortening of the electrochemical reaction time and thus lower quantitative yield of the redox change of the target analyte. On the other hand, lower flow rate in our selected buffer conditions probably caused higher dispersion of the sample zone over a wider area and the reaction was proceeded sufficiently [23]. The highest signals for all analyzed substances were obtained using the flow rate of 1.0 $mL.min^{-1}$ (Fig. 1). The flow rate of 1.2 $mL.min^{-1}$

exhibited overall decrease in the height of signals. Higher flow rate showed more decreasing trends in height of signals by all analyzed PGEs excepting $PtCl_4$, where only minimal difference between flow rate of 1.2 and 1.4 $mL.min^{-1}$ was observed. A decrease in the height of signals for individual PGEs was also observed at the flow rates lower than 1.0 $mL.min^{-1}$ (i.e. 600 and 800 $mL.min^{-1}$). That fact corresponds to the above-mentioned statement that lower flow rates and subsequently longer contact of the analyte zone with the surface of electrode can provide only larger areas of signals, not their heights [24]. In conclusion, the flow rate of 1.0 $mL.min^{-1}$ was found as the most suitable for further experiments and enables reduction in the consumption of reagents as well as decreasing of analysis time.

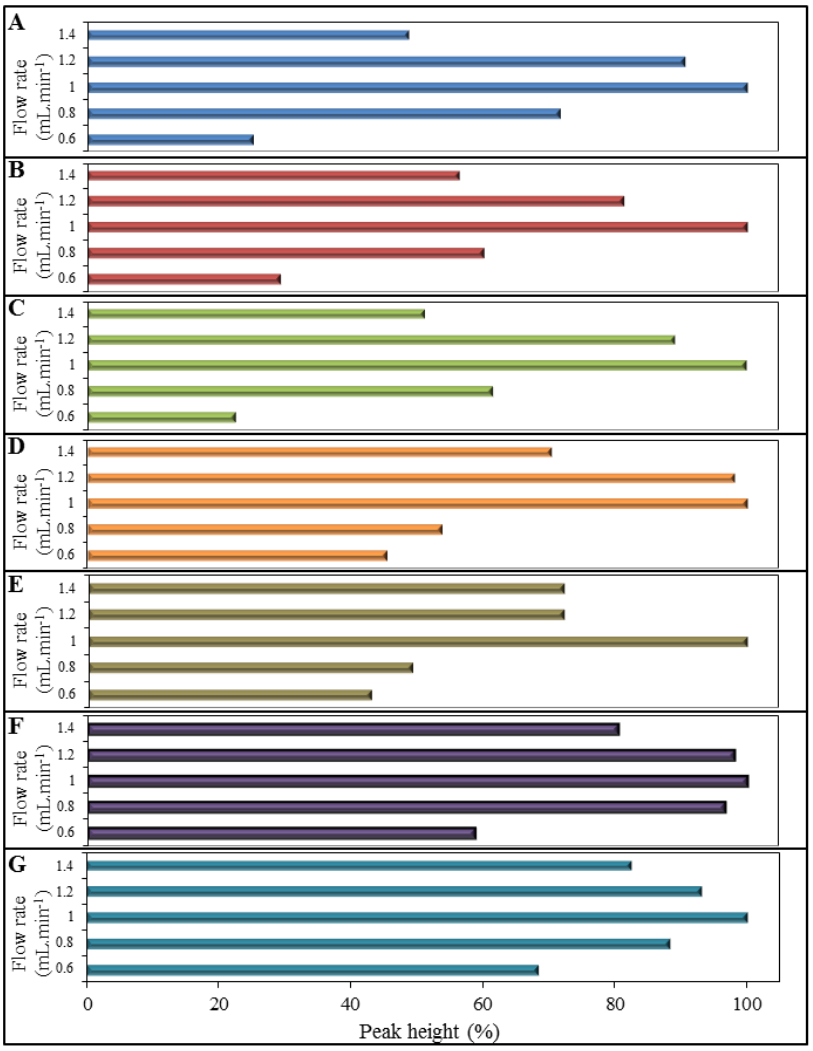

Figure 1. Flow rate optimization for each of PGEs using its ideal conditions obtained from buffer and potential optimization. Flow rate experiments were carried out with concentration of 10 $\mu g.mL^{-1}$ of (**A**) oxaliplatin in 4 pH acetate buffer with potential 1000 mV, (**B**) carboplatin in pH 4 acetate buffer with potential 1000 mV, (**C**) cisplatin in pH 4 acetate buffer with potential 1000 mV, (**D**) $PtCl_2$ in 3.5 acetate buffer with potential 1000 mV, (**E**) $PtCl_4$ in 3.5 pH acetate buffer with potential 1000 mV, (**F**) $RhCl_3$ in pH 7 borate buffer with potential 1100 mV, (**G**) $PdCl_2$ in pH 3.5 acetate buffer with potential 1100 mV.

3.2. Optimization of the applied potential and pH conditions

The sample in the mobile phase transformed physically and chemically into detectable species that cause a detector response downstream of the injection point. Therefore, it is clear that the value of pH of the supporting electrolyte has a major impact on the response in the most analytical determinations of both organic and inorganic compounds [25]. Due to the fact that we used different pH buffers as mobile phases, we were interested in the effects of pH on an electrochemical response of PGEs measured by a glassy carbon working electrode. Together with the pH, we also tested the effects of potentials applied onto the working electrode surface. Combination of both conditions should lead to find the optimal conditions for simultaneous determination of the tested PGEs and their compounds.

In order to evaluate this presumption, we selected acetate (Fig. 2A) and borate (Fig. 2B) buffers with an ability to maintain the constant conditions of the mobile phase during measurement (pH). The information from the hydrodynamic voltammograms helps us to characterize compound as a signal obtained in relation on applied potential during constant flow rate (Fig. 2).

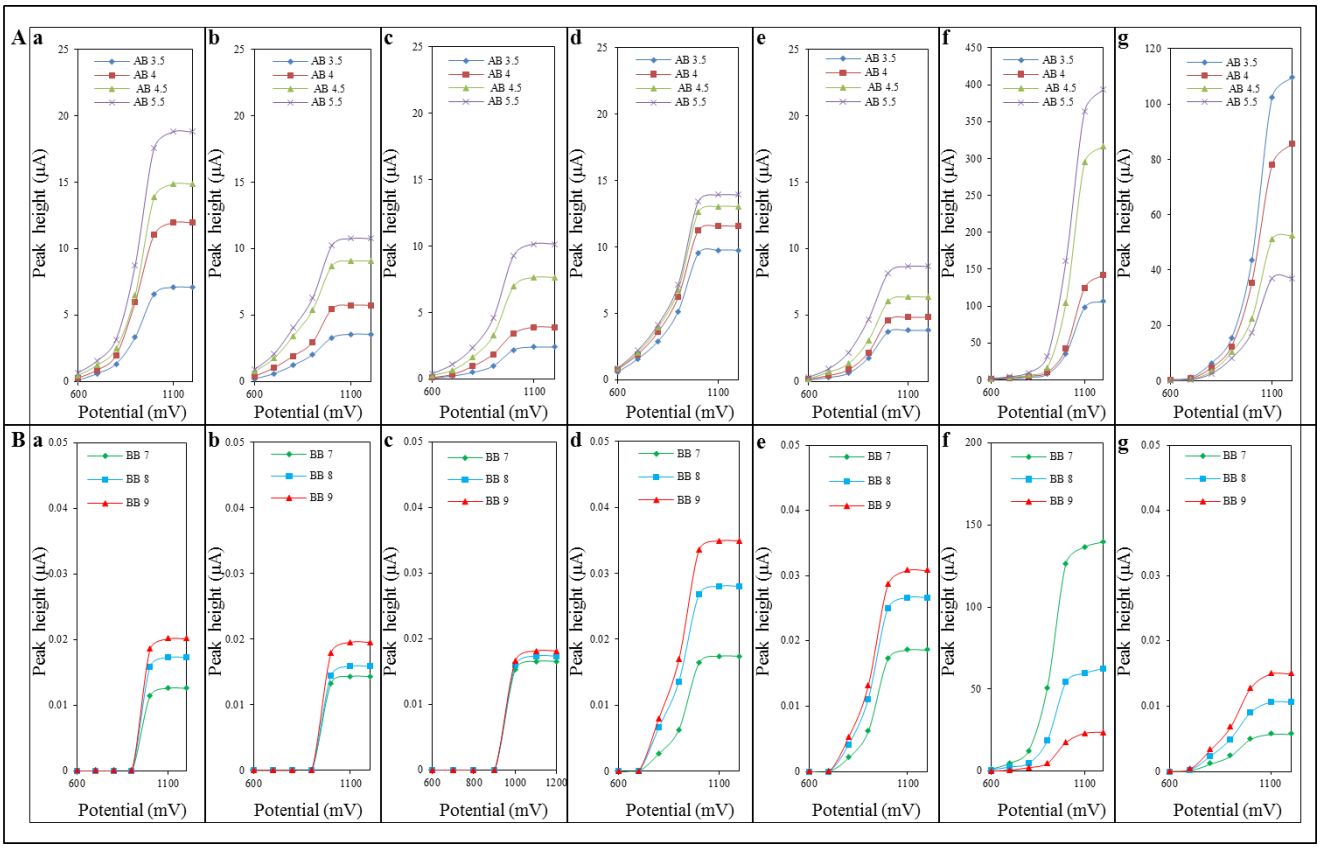

Figure 2. Hydrodynamic voltammograms (HDVs) of studied PGEs measured in the presence of two buffers as (**A**) acetate Buffer at pH 3.5, 4.0, 4.5, 5.5 and (**B**) borate buffer at pH 7.0, 8.0 and 9.0 respectively. All HDVs were carried out with concentration of 10 µg.mL^{-1} of PGEs. The measurements were performed for (**a**) oxaliplatin, (**b**) cisplatin, (**c**), carboplatin, (**d**) $PtCl_2$, (**e**) $PtCl_4$, (**f**) $RhCl_3$, (**g**) $PdCl_2$.

Thus HDVs helps us to select the condition in which the analyzed samples provide the largest signal. Primarily, we aimed our attention at acetate buffer of pH as 3.5, 4, 4.5 and 5.5. Under these conditions, oxaliplatin, cisplatin, carboplatin, $PtCl_2$, $PtCl_4$, $RhCl_3$ and $PdCl_2$ were analyzed and the obtained HDVs are shown in Figs. 2Aa, Ab, Ac, Ad, Ae, Af and Ag, respectively. The same was done in the presence of borate buffer (pH 7, 8 and 9) and the obtained HDVs are shown in Figs. 2Ba, Bb, Bc, Bd, Be, Bf and Bg, respectively. From the obtained results, it can be clearly concluded that the tested substances behave variously under constant conditions and this property may be very useful for their subsequent differentiation. As it is shown in raw hydrodynamic voltammograms, platinum compounds provide very weak signal in acetate buffer (Fig. 2Aa-e). In borate buffer, the signal of platinum substances was at the noise level as well as of palladium (Fig. 2Ba-e, Bg). On the other hand, rhodium provides very strong signal in both buffers (Fig. 2Af and 2Bf). These electrochemical properties of rhodium are further very helpful for its determination. Weak signal of platinum substances caused by their catalytic properties is bigger than that of rhodium and palladium. In this manner buffers were working as electrolytic binders [26] subjecting the PGEs to change their oxidation state causing higher electrodeposition and hence higher signal [27].

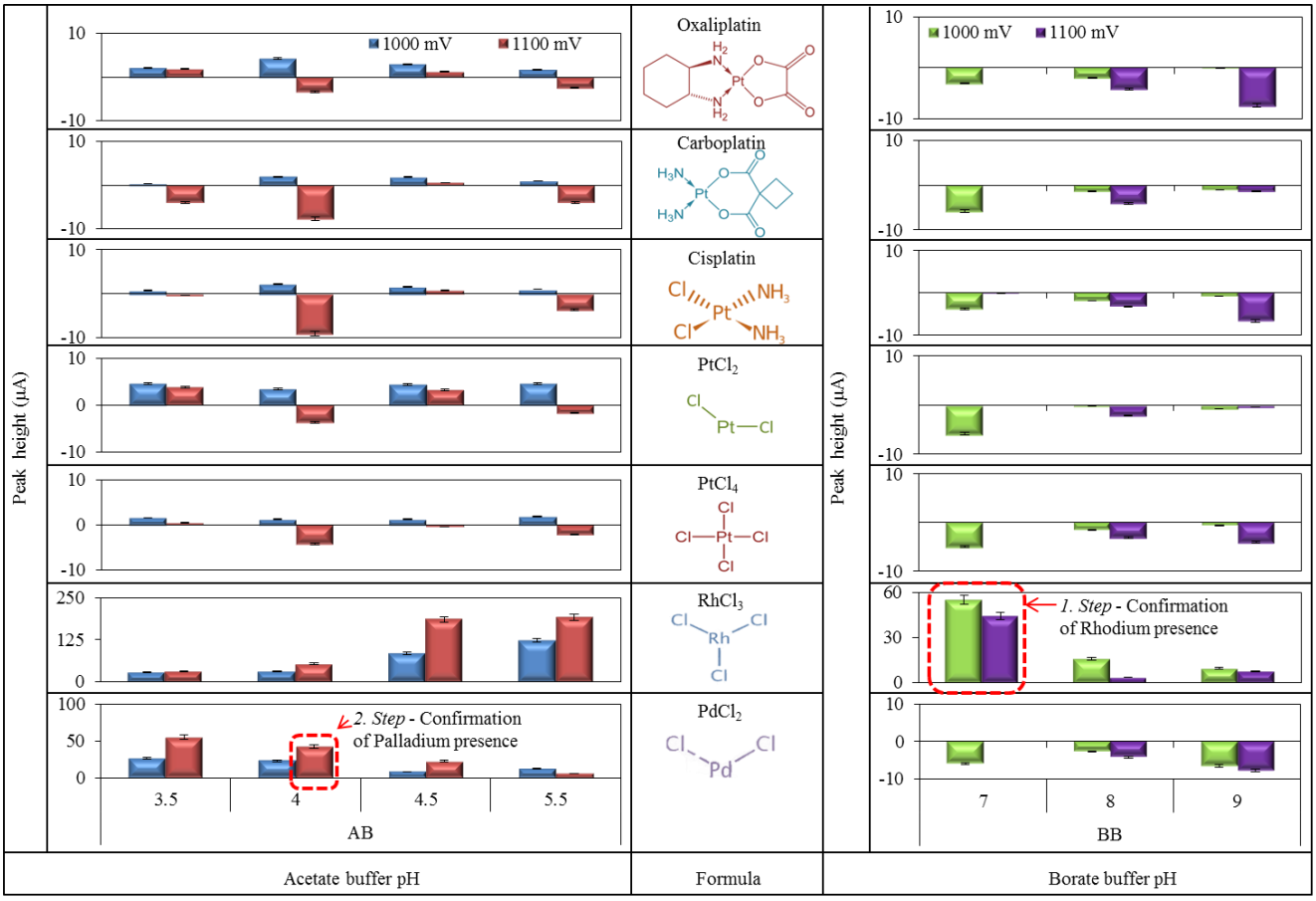

Figure 3. Expression of ideal potentials (range 1000-1200 mV) in both tested buffers (acetate buffer (AB), and borate buffer (BB)) for each of PGEs. Maximums were obtained from HDVs after data processing. All maximums were carried out with PGEs concentration of 10 $\mu g.mL^{-1}$. The most sensitive potentials were applied for **(A)** oxaliplatin, **(B)** carboplatin, **(C)** cisplatin, **(D)** $PtCl_2$, **(E)** $PtCl_4$, **(F)** $RhCl_3$ and **(G)** $PdCl_2$.

For better presentation of the results, we selected three potentials 1000, 1100 and 1200 mV, where the biggest changes were observed. After processing of raw data using subtraction of blank peak height from the peak height of analyzed PGE, results reporting the biggest changes are shown in Figs. 3A, B, C, D, E, F and G, for oxaliplatin, carboplatin, cisplatin, $PtCl_2$, $PtCl_4$, $RhCl_3$ and $PdCl_2$, respectively. The highest signal was given by rhodium as $RhCl_3$ in both buffering conditions. Increasing pH of acetate buffer led to an increase in the height of rhodium signal (Fig. 3F).

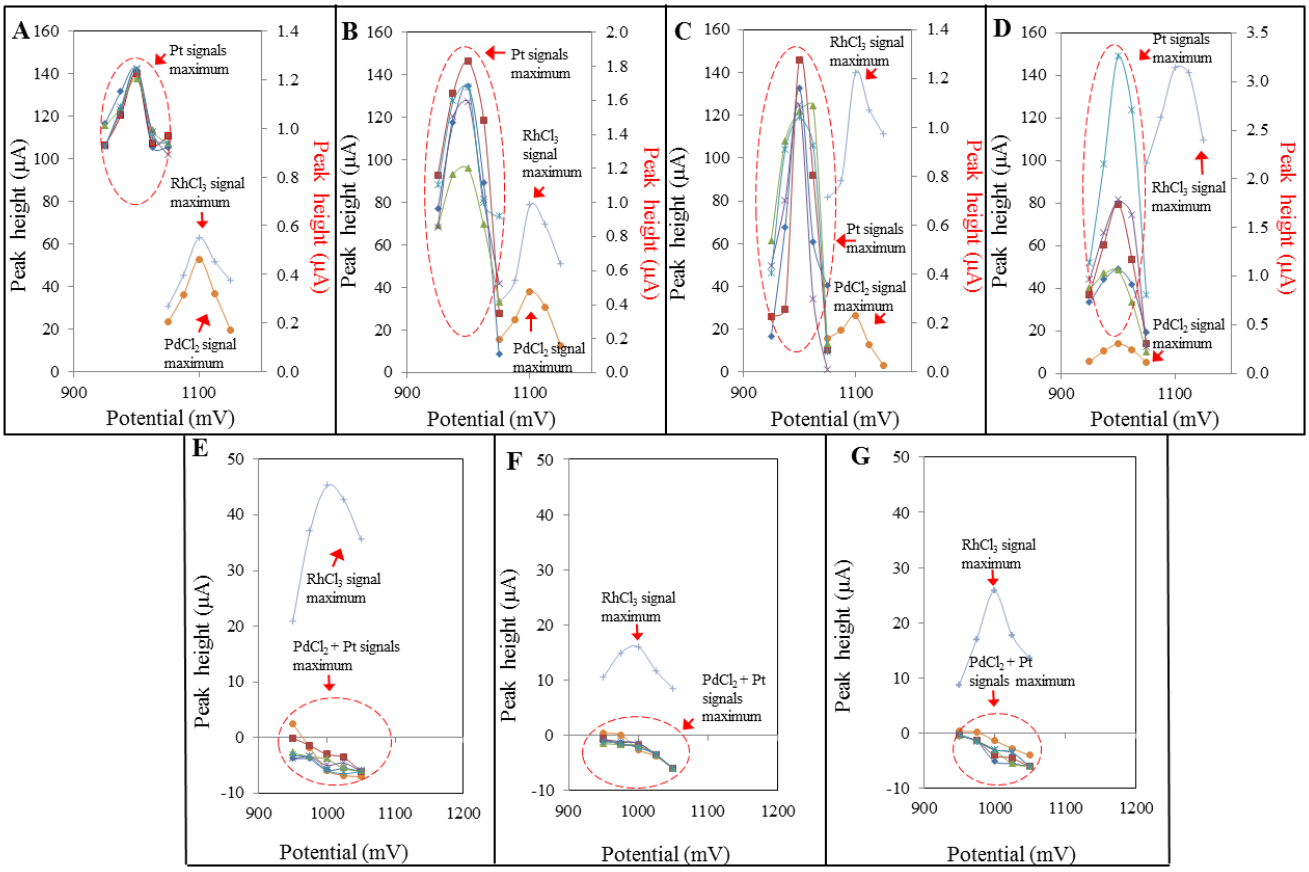

Figure 4. Representation of measuring of near potentials to the ideal one for all PGEs (oxaliplatin, cisplatin, carboplatin, $PtCl_4$, $PtCl_2$, $RhCl_3$, $PdCl_2$) in concentrations of 10 $\mu g.mL^{-1}$. (**A**) Acetate buffer of pH 3.5, (**B**) acetate buffer of pH 4, (**C**) acetate buffer of pH 4.5, (**D**) acetate buffer of pH 5.5, (**E**) borate buffer of pH 7, (**F**) borate buffer of pH 8, (**G**) borate buffer of pH 9.

On the other hand, in borate buffer with pH 7, rhodium showed the highest peaks and increasing pH had reducing effect on rhodium peak height. This points at the fact that pH is very important phenomenon in PGEs electrodeposition as well as buffer ionic strength. As the best potential applicable for rhodium analysis, 1100 mV was selected. This potential appeared to be most suitable also for palladium determination, nevertheless palladium shows different trend in electrodeposition influenced by buffer (Fig. 3G). The lowest pH used (pH 3.5) maintained the best conditions for palladium electrochemical analysis using GCE. By using borate buffer (all pH and all potentials

applied) for palladium analysis as well for platinum compounds (Fig. 3A-E) no observable peaks were obtained. This feature is useful for distinguishing between palladium and rhodium in our recognized hypothesis.

For reaching our main goal which was a rapid distinguishing between palladium and rhodium, we re-evaluated the results obtained and measured HDVs within the intervals from 950 to 1150 mV with potential step of 25 mV in great details (Fig. 4). This analysis was carried out as a confirmation of electrochemical behavior of PGEs. We were searching for an accurate potential applicable for the most precise measurement. The results of PGEs analysis in acetate buffer are shown in Fig. 4A-D. Platinum compounds are always circled in red oval. The most interesting finding was a potential shift in palladium analyzed using acetate buffer with pH 5.5 (Fig. 4D) instead of common 1100 mV. Probably, the increasing pH caused differences in oxidation state changes leading to decrease of potential value needed for palladium detection as it is confirmed in Fig. 4E-G. Other results obvious from Fig. 4 support the hypothesis about the possible distinction between PGEs based on the applied potential and buffer. Rhodium kept its ideal potential as 1100 mV in acetate buffer and 1000 mV in borate buffer. Platinum compounds showed that the possibility of their detection using this method is very complicated, because of no signal in borate buffer and very weak signal in acetate buffer. However this phenomenon is useful for rapid and simultaneous detection and determination of individual PGEs.

3.2.1 Borate buffer

Borate buffer of different pH values was used in our experiment as a first mobile phase for PGEs detection. Analysis performed by the use of borate buffer was shown to be crucial for the basic determination of $RhCl_3$. The most important relevance of the application of borate buffer consists in the fact that oxaliplatin, carboplatin, cisplatin, $PtCl_2$, $PtCl_4$, and $PdCl_2$ showed only minimal signals at any potential (Fig. 2Ba-g and Fig. 4E-G) unlike rhodium in $RhCl_3$ form. Hence, the borate buffer of pH 7 and potential of 1000 mV was selected to be crucial for the identification of rhodium. After the step with utilization of borate buffer of pH 7 and potential of 1000 mV was carried out, the result showed no signal and we may say that rhodium was not present in the analyzed sample. If some signal occurred then the presence of rhodium could be confirmed. In the case of negative signal, different experimental conditions are needed to detect palladium, as is shown below.

3.2.2 Acetate buffer

Acetate buffer seems to be the most suitable mobile phase for the PGEs analysis using various analytical methods as it was described in [23,28,29]. Applied potential of 1000 mV in combination with acetate buffer of pH 4 was determined to be the most advantageous in the analysis of oxaliplatin, carboplatin, cisplatin, $PtCl_2$, and $PtCl_4$. However these platinum compounds showed only weak signal slightly above the noise level under these conditions unusable for further analysis. On the other hand, results obtained in the same pH (pH 4) but with potential increased to 1100 mV were interesting, because no signal of platinum compounds was observed instead of palladium and rhodium (Fig. 3A-

G). In well agreement with these results, we selected the potential of 1100 mV in our experimental scheme. This potential provided no platinum and its compounds signal in buffer of pH 4. This phenomenon was proven to be useful for distinguishing of platinum and its compounds by palladium and rhodium that unlike platinum and its compounds showed good response at 1100 mV. Conditions maintained by acetate buffer of pH 3.5 showed higher signals for $PdCl_2$. This result is corresponding to the study by Castillo et al., who used acetate buffer of pH 3.2 for analysis of Pt, Pd, and Ir [29] but signal of platinum compounds under this pH was higher when compared with acetate buffer of pH 4 and it may be a complication for sensitive electrochemical analysis. Acetate buffer of pH 4 showed sufficient signals of palladium and therefore it was included into our determinative scheme for recognition of Pd from Rh.

3.3. Determination of PGEs based on the changes in potential and different pH

Table 1. Overview of the measurements of PGEs in the mixed samples spiked into water from Svratka River, prepared in various ratios. Rh – rhodium, Pd – palladium, Pt – platinum (cisplatin)

Mixture composition	Ratio of mixed PGEs	Concentration of mixed PGEs [µg.mL^{-1}]	Concentration determined [µg.mL^{-1}]	Deviation [%]
Rh : Pd	1 : 1	10 : 10	9	-10
Rh : Pd	1 : 10	10 : 100	10	0
Rh : Pd	1 : 50	10 : 500	9	-10
Rh : Pd	1 : 100	10 :1000	9	-10
Pd : Rh	1 : 1	10 : 10	9	-10
Pd : Rh	1 : 10	10 : 100	100	0
Pd : Rh	1 : 50	10 : 500	487	-3.6
Pd : Rh	1 : 100	10 :1000	940	-6
Rh : Pt	1 : 1	10 : 10	10	0
Rh : Pt	1 : 10	10 : 100	9	-10
Rh : Pt	1 : 50	10 : 500	10	0
Rh : Pt	1 : 100	10 :1000	10	0
Pt : Rh	1 : 1	10 : 10	10	0
Pt : Rh	1 : 10	10 : 100	99	-1
Pt : Rh	1 : 50	10 : 500	483	-3.4
Pt : Rh	1 : 100	10 :1000	963	-3.7
Pd : Pt	1 : 1	10 : 10	10	0
Pd : Pt	1 : 10	10 : 100	11	+10
Pd : Pt	1 : 50	10 : 500	10	0
Pd : Pt	1 : 100	10 :1000	9	-10
Pt : Pd	1 : 1	10 : 10	11	+10
Pt : Pd	1 : 10	10 : 100	98	-2
Pt : Pd	1 : 50	10 : 500	478	-4.4
Pt : Pd	1 : 100	10 :1000	979	-2.1

Light blue, violet, orange and green represent samples analyzed in borate buffer with pH of 9 - ideal conditions for determination of Rhodium. Two last blue labelled lines represent analyses carried out in acetate buffer with pH of 4, forming ideal conditions for determination of Palladium.

Simple and rapid determination of PGEs in water is very important due to the environmental load by these metals. Therefore, we suggested and designed the simple scheme, where $RhCl_3$ can be determined without difficulties in the first step. This first step is based on the application of borate buffer of pH 7 and the potential of 1000 mV, which leads to a positive response of electrochemical detector as it was mentioned above. The second step is proved after obtaining a negative signal and consists of the change of mobile phase from borate to acetate buffer of pH 4 and potential of 1100 mV. This positive response points at palladium presence. According to that fact our method was developed only for rapid qualitative analysis of PGEs, in which further speciation of individual PGE is less important such as industrial contamination or ecological catastrophes. The practical point of this method is based on possibility of the quick reveal of presence of PGEs in the analyzed sample, which can be further subjected to a precise quantitative analysis. The analytical methods such as atomic absorption spectrometry [30,31], atomic emission spectrometry [5,15] or detection by mass spectrometry [29,32] can be subsequently used for such purpose. However, application of such methods takes is more time-consuming and is usually more expensive. It clearly follows regarding to economical and practical aspects that our method could be used for first step low-cost analysis.

3.4. Analysis of mixed PGEs in real sample of water

Table 1 shows the results of analysis of mixed samples prepared in different ratios. The real sample of water, obtained from river Svratka was spiked with known concentration of PGEs mixture in different ratios, as is mentioned in chapter Mixed samples preparation. It was confirmed that our determinative scheme may be applied for determination of PGEs. In addition, accuracy of analysis is sufficiently close to the real concentrations, which were used (Deviation $\leq$ 10 %). In the both buffers used (borate buffer with pH 7 for rhodium determination; acetate buffer with pH 4 for palladium determination), platinum compounds exhibited no signal. This fact was the confirmation for us that our scheme is applicable. According to the calibration curves, the signals of Pd and Rh in the mixtures correspond and therefore it is clear that the signal was not affected by the presence of another PGE in the mixture. Although, according to calibration curves ($y = 13.9922x + 3.0141$, $R^2 = 0.9821$ for Rh, $y = 10.5332x + 0.4921$, $R^2 = 0.9914$ for Pd), limits of detection were established to 150 $ng.mL^{-1}$ for Rh and 210 $ng.mL^{-1}$ for Pd and levels of contamination of surface waters is far from reaching our values, our method may serve as a very fast screening of presence of Rh or Pd in water after some unfortunate events, leading to timely implementation of security measures.

4. CONCLUSION

The flow injection analysis connected with an electrochemical detection, which uses a flow cell with a GC electrode, provides a possibility of obtaining the hydrodynamic voltamograms of palladium

and rhodium in a short time. We performed an automatic and rapid analysis of PGEs in water using different values of pH that was adjusted by suitable buffers. Optimal conditions of the analysis of PGEs have been determined and then used for distinguishing between palladium and rhodium from other PGEs. Flow injection method developed by us is based on differences in behavior of PGEs at their redox potentials at varying conditions maintained by the buffers. Whole optimized method can thus serve for determination of PGEs as the hazardous pollutants of water based on different pH values, with LoDs of 200 $ng.mL^{-1}$ for Rh and 300 $ng.mL^{-1}$ for Pd. This selective, robust and rapid method may serve for screening of sudden contamination of environment. The results of this study may be also helpful for development of various electrode modifications as a next important step in quantification of platinum compounds that can effectively lower the limit of detection in given type of sample (matrix).

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